GUIDING PRINCIPLE TO DEVELOP INTRINSIC MICROCRYSTALLINE SILICON ABSORBER LAYER FOR SOLAR CELL BY HOT-WIRE CVD

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ABSTRACT

We report on ways to develop device quality microcrystalline silicon (μc-Si:H) intrinsic layer with high growth rate by hot-wire chemical vapor deposition (HWCVD). With combine approach of controlling impurities and moderate H-dilution [$H_2/SiH_4 \approx 2.5$], *we developed, for the first time, highly photosensitive (10^3) μc-Si:H films with high growth rate (>1 nm/s)*; the microstructure of the film is found to be close to amorphous phase ($f_c \approx 46 \pm 5\%$). The photosensitivity systematically decreases with f_c and saturates to 10 for $f_c > 70\%$. On application of these materials in non-optimized pin μc-Si:H solar cell structure yields 700 mV open-circuit voltage however, surprisingly low fill factor and short circuit current. The importance of reduction of oxygen impurities [O], adequate passivation of grain boundary (GB) as well as presence of *inactive GB* of (220) orientation to achieve efficient μc-Si:H solar cells are discussed.

INTRODUCTION

Since the report on 7.7% single junction microcrystalline silicon (μc-Si:H) solar cells and 13.1% a-Si:H/μc-Si:H tandem cells by University of Neuchatel in 1996, the low-temperature microcrystalline solar cells technology has taken significant stride over last five years [1]. Recently Kaneka Corporation, Japan has demonstrated a-Si:H/poly-Si tandem solar cells at $550^{°}C$ substrate temperature with 11.6% initial and 9.2% stable module efficiency (910 x 455 mm^2) using unknown modified PECVD [2]. However both Neuchatel group and Kaneka Corporation have been investigating without much success to increase the growth rate of microcrystalline and polycrystalline films more than 0.1 nm/s, so that the entire device can be fabricated within reasonable time. On the other hand, in last five years hot-wire CVD appeared as a low-cost technique for one-step deposition of microcrystalline and polycrystalline thin films with high growth rate (> 1.5 nm/s) on low cost substrate like glass [3]. In addition scale-up potential of HWCVD has also been demonstrated [4]. Thus with proper control of materials engineering and device technology, HWCVD should be a promising technique for the fabrication of low cost thin silicon film solar cells both from throughput and capital cost point of view. Here we report our effort to develop high growth rate device quality μc-Si:H absorber layer and solar cells so that it can be integrated into our a-Si:H/a-Si:H tandem-junction solar cells technology [5] as a bottom cells to increase short circuit current and hence overall efficiency of the tandem devices.

EXPERIMENTAL DETAILS

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In this work an ultra-high vacuum (10^{-7} mbar) multi-chamber hot-wire chemical vapor deposition system have been used to prepare films and solar cells. In the intrinsic chamber in-situ ellipsometer is attached to study the initial growth process of amorphous and microcrystalline silicon thin-film on glass substrates. Both base vacuum as well as process pressure has been maintained by a turbo molecular pump. Tantalum wire have been used as heated catalizer, specific filament geometry and filament holder have described in details elsewhere [6]. With improved filament mounting and handling procedure, we do not face any filament breakage
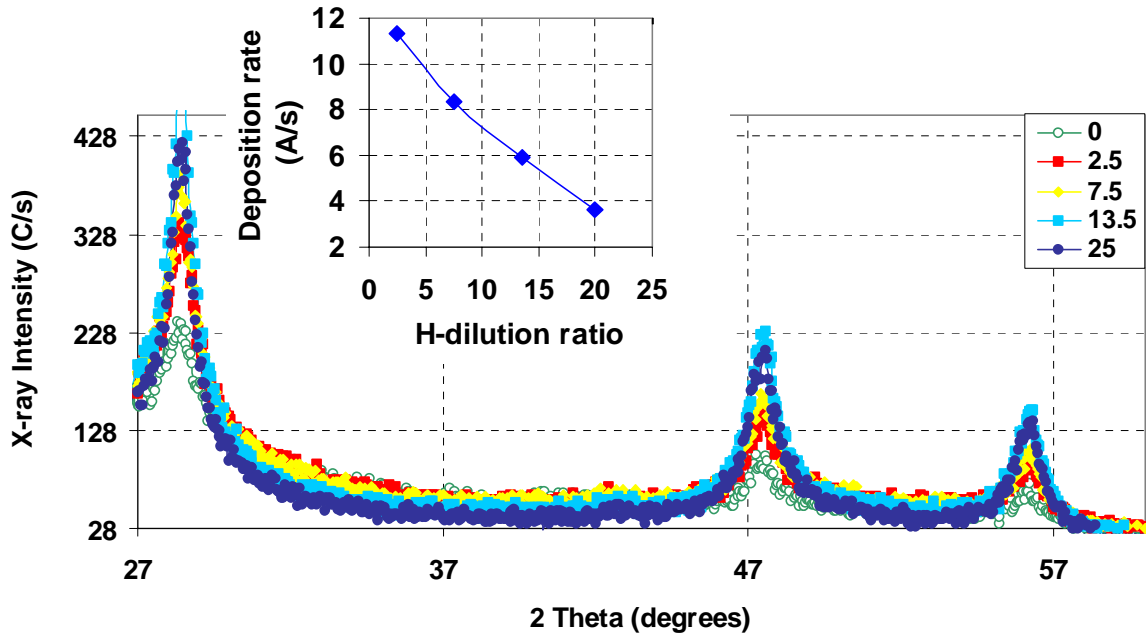

Fig. 1: XRD pattern of microcrystalline Si films prepared with different H-dilution.

problem. The temperature of the filament has been measured by two wavelength optical pyrometer. The leak rate of the reactor has been studied both filament on and off condition and the estimated the leak rate is 2×10^{-7} mbar/sec when filament at 1800°C. So the out-gassing of the reactor wall is low during film preparation. Gas purifiers are attached in all process gases to minimize the contamination from source materials. In addition we followed a very special procedure to reduce the residual water vapor (H_2O) in the reactor and to minimize further the out-gassing from the reactor wall. For all the films, the chamber pressure, the filament-to-substrate distance, the filament and the substrate temperature have been maintained at 150 mTorr, 2 cm, 1750°C and 200°C respectively. The hydrogen to silane flow ratio has been varied from 0 to 25 to prepare films with fully amorphous to microcrystalline films with high crystalline component. During solar cells fabrication, boron-doped (from trimethyl boron) amorphous silicon carbide or microcrystalline silicon films is deposited first on SnO_2 or ZnO-coated glass substrate then intrinsic microcrystalline layer followed by n-type microcrystalline silicon layer. Finally aluminum metal contact has been evaporated on top of n-layer. Films have been characterized by dark and photoconductivity measurement and photothermal deflection spectroscopy. The photoconductivity measurement has been performed under He-Ne laser ($\lambda \approx 633$ nm) with photon density 10^{16} $cm^{-2}sec^{-1}$. The phase of the materials and relative component of amorphous and crystalline part have been analyzed by X-ray diffraction using fitting procedure.
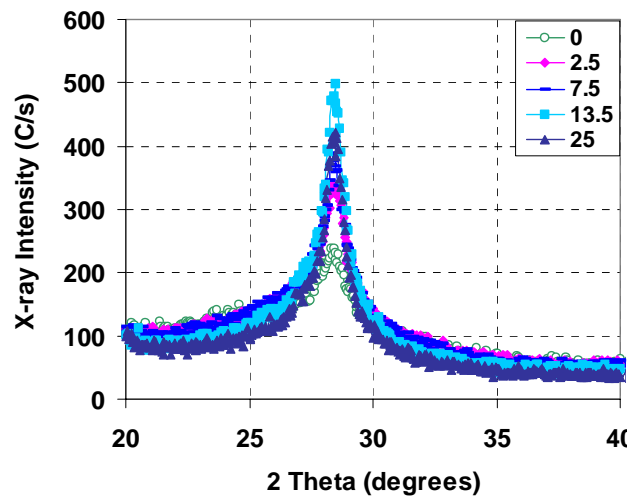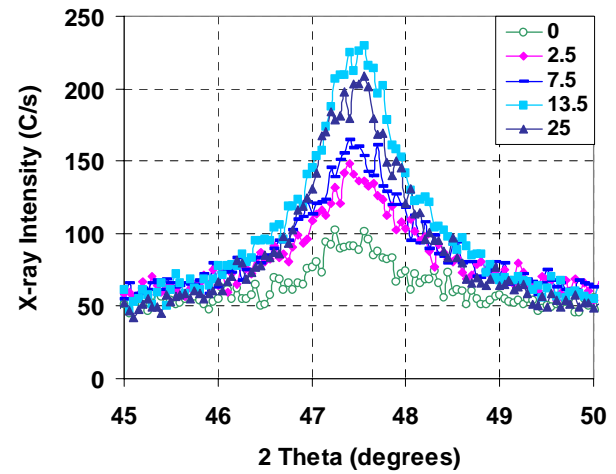
Fig. 2(a): Comparison of FWHM of (111) XRD peak.

Fig. 2(b): Comparison of FWHM of (220) XRD peak.

RESULTS AND DISCUSSION

 Fig. 1 shows the XRD patterns of films prepared with increasing H-dilution (0 to 25). All the films are microcrystalline with (111), (220) and (311) crystallographic planes even when H-dilution is zero. It means that the specific deposition condition we have chosen, decomposition of silane in the heated catalyzer is so high that normalized H-flux, $H/(SiH_X)$, X=1-3, arriving at the substrate is high enough to grow microcrystalline films. However all the films have powder diffraction pattern, no preferential orientation of crystallographic planes has been observed. By fitting XRD spectrum, amorphous and crystalline fraction were estimated. It has been observed that H-dilution critically controls the crystalline fraction in the materials, which will be discussed latter. The inset of Fig.1 exhibits the variation of deposition rate (R_d) of the films with H-dilution ratio, R_d monotonically decreases with H-dilution, however at low dilution (< 4), R_d is more than 1 nm/s. We looked into XRD pattern more closely to find out effect of H-dilution on crystallographic structure of the films. Fig. 2(a) show comparison of full-width-half-maximum (FWHM) of (111) peak of XRD pattern of films prepared with different H-dilution. We did not attempt to calculate crystal size either from the linewidth of (111) or (220) peaks since narrowing of linewidth involves lot of things in addition to it's linearly correlation with the crystal size. In fact there is no physical meaning of "crystal size" in low-temperature microcrystalline silicon, the number we get using FWHM of XRD peak corresponds to equivalent length of defect-free crystals. However variation of linewidth is unambiguously correlated with the improvement or deterioration crystallographic quality of the films which might have link with its electronic property as a absorber layer. It may be noted from Fig. 2(a) that FWHM of (111) peak decreases with increasing H-dilution, similar trend is also observed for (220) peak as shown in Fig. 2(b). Thus with increase H-dilution overall crystalline quality (reduction of extended defects and or enlargement of defect-free crystal size) of microcrystalline silicon films improves. When we look into their corresponding electronic properties it surprises us. The variation of dark and photoconductivity of films prepared with different H-dilution is shown in Fig. 3. The dark conductivity (σ_d) increases monotonically upto H-dilution of 5 then it saturates around 10^{-6} S/cm. The photoconductivity(σ_{ph}) under monochromatic light first increases slightly to a maximum
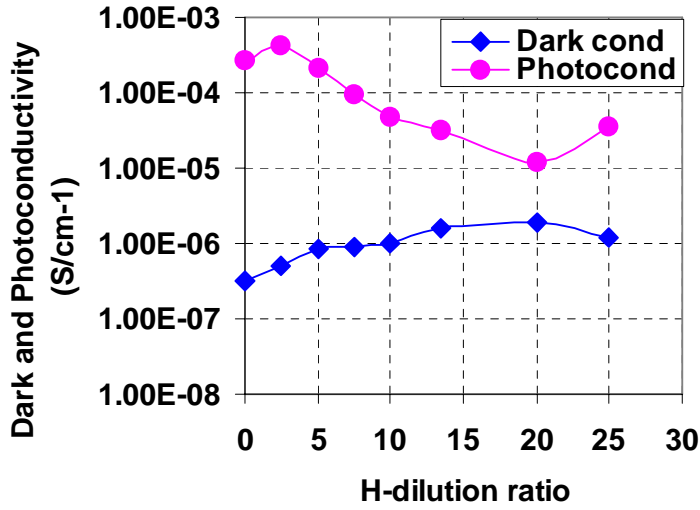
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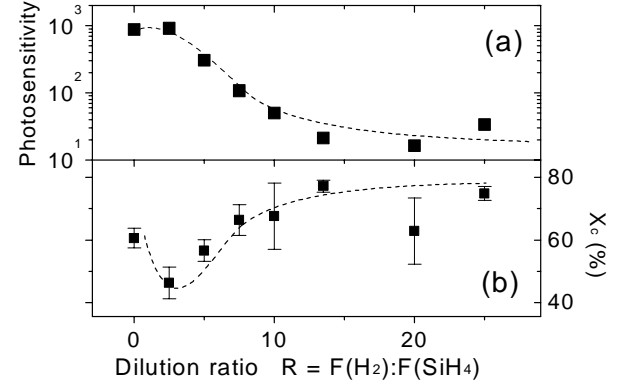Fig. 3: Variation of dark and photoconductivity with H-dilution ratio

Fig. 4: Variation photosensitivity and crystalline fraction with H-dilution ratio.

value $\sim 5 \times 10^{-4}$ S/cm for H-dilution ≈ 2.5 and then decreases monotonically to 10^{-5} S/cm. For H-dilution higher than 15, σ_{ph} remains more or less constant around 10^{-5} S/cm. The photosensitivity (σ_{ph}/σ_d) also varies monotonically with H-dilution as shown in Fig. 4. For low H-dilution (< 2.5), $\sigma_{ph}/\sigma_d \approx 10^3$ and then steadily decreases with increasing H-dilution and finally saturates to 10 for H-dilution more than 20. In the same graph (Fig. 4), variation of f_c estimated from XRD has been plotted versus H-dilution. The f_c drops from 50% to 46% as H-dilution is increased from 0 to 2.5, then it increases exponentially and saturates at 70 to 80% for H-dilution higher than 15.

Table I: pin microcrystalline silicon solar cells parameters versus photosensitivity of absorber layer.

Cell #	$S = \sigma_{ph}/\sigma_d$ of i-layer	V_{oc} (mV)	FF	J_{sc} (mA/cm^2)	Effn. (%)
MSi-1-1	10^3	0.674	0.211	7.51	1.07
MSi-1-2	10^3	0.697	0.241	2.91	0.49
MSi-1-3-1	10^3	0.683	0.258	8.38	1.48
MSi-1-3-1	**10^3**	**0.696**	0.248	6.63	1.14
RSU-7-1	10	0.505	0.226	0.7	0.08
RSU-11	10	0.454	0.292	2.01	0.27

Except the initial drop of f_c, both σ_{ph} and σ_{ph}/σ_d systematically follows the trend of variation f_c versus H-dilution. The highest σ_{ph} is obtained when f_c is lowest (H-dilution. ≈ 2.5) and as f_c increases, σ_{ph} decreases and also σ_{ph}/σ_d steadily decreases from 10^3 to 10 as f_c increase from 46 $\pm$ 5% to 75%. Thus the highest photoconductivity and photosensitivity are obtained when f_c is lowest (46%). In other words, for optimum absorber layer, crystalline fraction should be low, i.e. grain boundary should be well passivated by the amorphous phase.

The high photoconductivity as well as photosensitivity of absorber layer does not automatically

qualify it as an best intrinsic layer for solar cells. So we attempted to fabricate solar cells using the optimized absorber layer ($\sigma_{ph}/\sigma_d \approx 10^3$). On application of the materials in unoptimized pin solar cells structure, surprising results has been obtained, i.e. V_{oc} was high (as high as 700 mV) but fill factor (FF) and short circuit current (J_{sc}) were low. The satistics of the solar cells results has been summarized in Table I. It may be noted from Table I that V_{oc} varies 670 to 700 mV whenever the photosensitivity of the absorber layer is 10^3. In μc-Si:H solar cells, highest V_{oc} value obtained so far around 550 mV. Thus, one possible way to improve V_{oc} of μc-Si:H solar cells is to improve σ_{ph}/σ_d of the absorber layer and this is fully consistent with qualitative quasi Fermi level splitting model of V_{oc} , it depends on splitting of quasi Fermi level of electron and holes. From Table I it is also evident that J_{sc} is proportional to σ_{ph}/σ, when σ_{ph}/σ is 10, J_{sc} of the order 1 to 2 mA/cm^2 versus 6 to 8 mA/cm^2 for high photosensitive samples (except the sample MSi-1-2). It should be mentioned that J_{sc}, ($\approx$ 6 to 8 mA/cm^2) of devices of Table I is much lower than 22 to 25 mA/cm^2 normally observed best μc-Si:H solar cells [7]. Moreover, FF of all the devices were low, indicating that either there is some problem in the p-layer or p/i interface or transport of carriers across i-layer towards end of the electrode. Since V_{oc} value we obtained, higher than the best value reported in the literature which is also consistent with its high photosensitivity, we can not identify p-layer or p/i interface is not the cause of low FF, it should be related to the carrier transport in intrinsic layer during forward bias solar cells operating condition. We believe that the poor FF and low J_{sc} in our solar cells are related to the lack of preferential orientation of (220) orientation with inactive grain boundary. Based on the data on microcrystalline films and solar cells we propose following quasi-one dimensional carrier transport model in low-temperature μc-Si:H solar cells.

During photon harvesting time (solar irradiation) in mixed phase μc-Si:H films, total photogenerated carriers is much higher within the small crystallites than neighbouring amorphous Si because of lower bandgap (1.1 eV) of crystalline Si. The carriers immediately diffuse to the surrounding amorphous matrix. If the defect density of the amorphous part or at the grain boundary is high, the diffused photogenerated carriers will immediately recombine and this process will continue until most of the carriers are lost in recombination. If on the other hand, the defect density in amorphous and GB is low then they will act as a reservoir of traps of photogeneration carriers. Once these traps are filled, then remaining carriers inside the grains will diffuse through crystalline part along the film growth direction to be collected at the other end of the electrode of solar cells. During this transit time, carriers will encounter numerous defects and impurity centers in c-Si materials. At this juncture several possibilities may happen: I. if O-impurity is very high, most of the carriers will recombine in the notorious SiO_2-related defect complex in c-Si [8], II if the orientation of crystalline planes are random, such as in our samples, carriers will encounter various types of classical extended defects at the boundaries between different unit cells. However, if (220) preferential orientation exists along the growth direction, carriers will face least recombination centers while traversing towards other electrode of solar cells. The density of twins and dislocation even in (220) planes should be also low to minimize the carrier recombination during its transport. Recent report [7] on influence of surface morphology of transparent conducting oxide (TCO) on subsequent columnar film growth and hence on microcrystalline silicon solar cells clearly illustrate that the orientation of the crystallographic planes parallel to film growth direction helps transport of photogenerated carriers towards other end of the electrode of solar cells. Thus the carrier transport in low-temperature μc-Si solar cells is almost like one-dimensional, along (220) orientation in film growth direction. The model presented here is consistent with the results of the best

microcrystalline silicon solar cells reported in the literature. The solar cells parameters ($V_{oc} \approx$ 500 to 600 mV, $J_{sc} \approx$ 22 to 25 mA/cm^2) suggest without ambiguity that photocarrier generation and transport are predominantly occurring inside the grain, although recombination in amorphous phase and GB limit the entire carrier transport process. Based on our present understanding, the guiding principle to develop low-temperature microcrystalline silicon absorber layers are: 1. GB should be well passivated by amorphous phase (f_c should be < 50%), 2. defect density of amorphous component should be low (< 10^{16} cm^{-3}), 3. oxygen content should be below certain limit (<10^{19} cm^{-3}), 4. there should be (220) preferential orientation in c-Si component.

CONCLUSIONS

We developed, for the first time, a highly photosensitive (10^3) μc-Si:H films with high growth rate (> 1 nm/s) by hot-wire CVD with a combine approach of controlling impurities and microstructure of the film. We conclude, for low-temperature optimum microcrystalline Si absorber layer, the microstructure of the film should be close to amorphous phase, i.e. GB should be well passivated. On application of the highly photosensitive intrinsic layer in non-optimized pin μc-Si:H solar cell structure yields 700 mV open-circuit voltage however fill factor and short circuit current are low. Based on our data and results reported in the literature, we postulated a quasi-one-dimensional carrier transport model of low-temperature microcrystalline Si solar cells.

ACKNOWLEDGEMENTS

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